Intra-pulse Cavity Enhanced Measurements of Carbon Monoxide in a Rapid Compression Machine

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Abstract: A laser absorption sensor for carbon monoxide concentration was developed for combustion studies in a rapid compression machine using a pulsed quantum cascade laser near 4.89 μm. Cavity enhancement reduced minimum detection limit down to 2.4 ppm at combustion relevant conditions. Off-axis alignment and rapid intra-pulse down-chirp resulted in effective suppression of cavity noise.
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1. Introduction

Rapid compression machines (RCMs) are important tools for investigating ignition characteristics of hydrocarbon fuels at conditions relevant to low-temperature oxidation chemistry (700 – 900 K, 10 – 40 bar) [1]. RCMs provide a nearly isentropic, homogeneous environment for evaluating chemical kinetic models of low-temperature combustion. Validation of such models requires time-resolved concentration measurements of intermediate species, such as carbon monoxide (CO) [2]. Moreover, to maintain a uniform temperature field during the experiment, dilute reactant gas mixtures must be used to reduce magnitude of heat release, thus increasing sensitivity demands on concentration sensors. In this work, we report the application of a mid-IR laser sensor based on cavity enhanced absorption spectroscopy (CEAS) for CO detection in an RCM. The sensor provides significant improvement in minimum detection limit over single-pass direct absorption.

2. Sensor Description

A distributed feedback quantum cascade laser (DFB-QCL), described previously in [3], was used in pulsed mode to probe the P(23) molecular transition of CO near 4.89 μm. The laser was aligned in an off-axis arrangement with a cavity mounted on the RCM combustion chamber. The RCM, details of which can be found in [3], has an inner diameter of 5.08 cm which serves as the single pass path-length. Two CaF_2 concave mirrors, sourced from RMI Co. with a nominal reflectivity of 99.5%, were used to form the cavity. The laser signal was recorded on a 500 MHz bandwidth MCT detector from Vigo System, and acquired at 100 MHz sampling frequency by an oscilloscope.

The QCL was operated at 100 kHz repetition rate with a 500 ns pulse duration. This provided rapid intra-pulse down-chirp, averaging 6.52 $cm^{-1}/\mu s$, as measured using a Germanium etalon. The rapid frequency scan coupled with the off-axis alignment resulted in cavity noise being effectively suppressed, as illustrated by the laser intensity trace in Fig. 1 (right). The single pass absorbance A_{SP} is related to the CEAS absorbance *via* $A_{CEAS} = \ln(1 + GA_{SP})$. In turn, using spectroscopic parameters from HITRAN [4], the species mole fraction X can be inferred from the Beer Lambert relation: $A_{SP} = (SPXL\Phi_v)$. In static cell measurements with known CO/N_2 mixtures, the gain factor G was found to be 133 ± 8, thus the measured mirror reflectivity is 99.25 ± 0.04%.

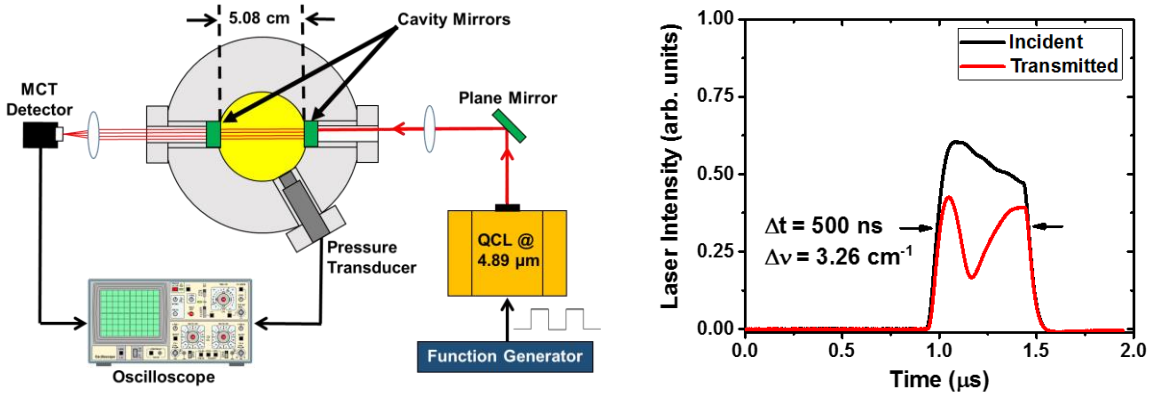

Fig. 1. **Left:** Optical Schematic of CEAS sensor aligned on the cross-section of the RCM combustion chamber. **Right:** Laser intensity trace for static cell measurements at 80 ºC, 7 bar.

3. Experimental Results

Figure 2 (left) shows simulated comparison of detection limits between CEAS and single-pass arrangements for the P(23) CO line at typical RCM conditions. At 800 K, the CEAS technique produces a reduction in the minimum detection limit by factor of 63 (2.4 ppm down from 151 ppm).

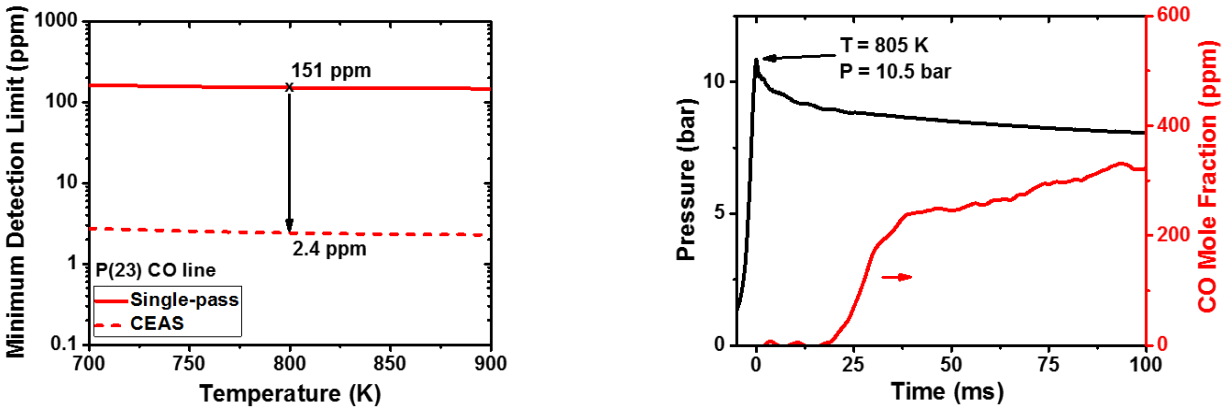

Fig. 2. **Left:** Minimum detection limit of CO using P(23) absorption line. **Right:** Measured CO concentration and pressure profile for the oxidation of 0.2% *n*-octane / 2.5% oxygen / 97% nitrogen.

The sensor was used for measuring CO species time-histories for *n*-octane oxidation as shown in Fig 2 (right). The measurements have an effective time resolution of 10 μs over a total measurement time window of 100 ms, the typical residence time for most RCM facilities. High frequency noise from pulse-to-pulse variations as well as sampling bit noise from the oscilloscope was removed from the CO profile using a 2 kHz low-pass filter in post-processing. Time zero for the pressure trace is set to the end-of-compression phase, which in this case occurs at the maximum point of the measured pressure trace. The onset of CO formation at about 25 ms corresponds to the low-temperature first-stage ignition. For stoichiometric *n*-octane/air mixtures (i.e., φ=1), 1.65% mole fraction of *n*-octane is required in the gas mixture. Here however, only 0.2% *n*-octane was used, significantly reducing reactivity and suppressing heat release, as is evident from the pressure trace in Fig. 2 (right). Such measurements in dilute mixtures are highly useful for validation the low-temperature reaction kinetics.

3. Conclusions

A laser sensor based on the CEAS technique was demonstrated for CO measurements in an RCM. The sensor provided high time resolution (10 μs) as well as more than an order of magnitude higher sensitivity than a conventional single-pass absorption technique. The decreased detection limit allows for dilute reactive mixtures to be used for validating kinetic models, ensuring a reactive system free from transport effects.

4. Acknowledgements

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5. References

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